

oil. In 1950, vitamin A was commercially synthesized,<sup>17</sup> and this process has made a sizable dent in the market formerly held by fish-liver oils. This 12-step synthesis process is based on citral, formaldehyde, and acetic acid as raw materials. See Vitamins, Chap. 6.

**Fish oils.** Fresh menhaden,<sup>18</sup> sardine, and salmon are cooked whole by steaming for a short period and pressed. The oil is settled (or centrifuged) and winterized. The remainder of the fish is dried, pulverized, and sold as meal for feed. Each fish contains, on the average, 20% oil by weight. The oils are consumed in paints, as lubricants, and in leather and soft-soap manufacture, and when sulfonated yield a variety of turkey-red oil.

The tremendous quantities of *butter* and *tallow* produced for food in the United States are shown in Fig. 2.1. Tallow is rendered similarly to lard, and butter fat is obtained by centrifugal separators.

**Lard.** Lard and lard oil are the most important animal fats and are produced by the rendering of hog fat. Lard oil is the most important of the animal oils and is expressed from white grease, an inedible lard. Lard has been fundamentally upgraded by modern chemical conversions, interesterification and isomerization, which are discussed later.

## Processing

**ISOMERIZATION REACTIONS.** In addition to the formation of more saturated compounds during hydrogenation (Figs. 2.5 and 2.6), the reaction may be accompanied by the formation of isomeric unsaturated fatty acids. These may be positional isomers resulting from the migration of double bonds, or geometric (spatial) isomers resulting from the conversion of naturally occurring *cis* forms to *trans* forms. These isomers are of considerable interest, chiefly because of their different physical properties. There is also evidence that the rate of hydrogenation of the different isomers varies, so that their presence affects the overall reaction rate and final composition.<sup>19</sup> One explanation of isomerization is based on the half-hydrogenation-dehydrogenation sequence. During hydrogenation a hydrogen atom can add to either end of the double bond and form a free-radical center, probably still attached to the catalyst. This free-radical center is quite unstable, and if a catalyst is only partially covered with hydrogen, a hydrogen atom may be eliminated from a carbon next to the free-radical center, re-forming the double bond. In this way either a positional isomer is formed or the bond in the initial position is regenerated. Since the formation of a free-radical center allows free rotation, the new unsaturated compound is able to be formed in a *cis* or *trans* configuration, according to the thermodynamic stability of each form. Experimental evidence suggests a *trans*-oleic (elaidic)/*cis*-oleic equilibrium ratio of at least 2:1.<sup>20</sup>

To summarize: "The food fat processor can purify to a high degree the natural crude oils. He can change the character of the side chain fatty acids by hydrogenation, and change their relative positions in the triglyceride randomly or controllably by interesterification. He can create solids *in situ*, add them or remove them, and have them assume a stiffening or non-stiffening character. With such flexibility he is providing the public with a variety of palatable and nutritious foods; and if the need arises for fats with special nutritional properties, he has the means to produce them."<sup>21</sup>

<sup>17</sup>O'Connor, Synthetic Vitamin A, *Chem. Eng.* 57 (4) 146 (1950).

<sup>18</sup>Stansby, *Fish Oils*, Avi, Westport, Conn., 1967.

<sup>19</sup>Allen and Kiess, *J. Am. Oil Chem. Soc.* 33 355 (1956).

<sup>20</sup>For details see James, *Homogeneous Hydrogen*, Wiley-Interscience, New York, 1975.

<sup>21</sup>Sanders, Processing of Food Fats, *Food Technol.* 13 (1) 41 (1959).

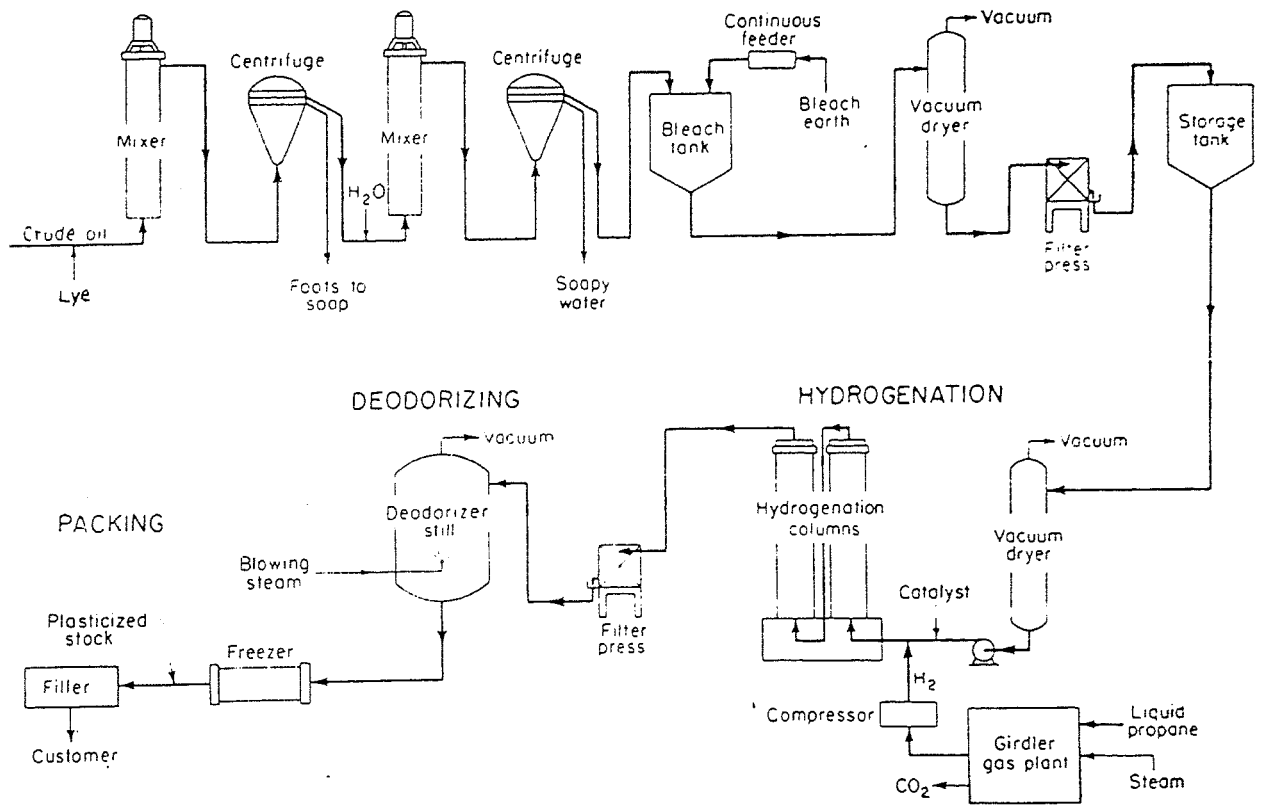


Fig. 2.5. Flowchart for continuous processing of edible oils, either vegetable or animal, including refining, bleaching, hydrogenation, and deodorizing. (Procter & Gamble Co.)

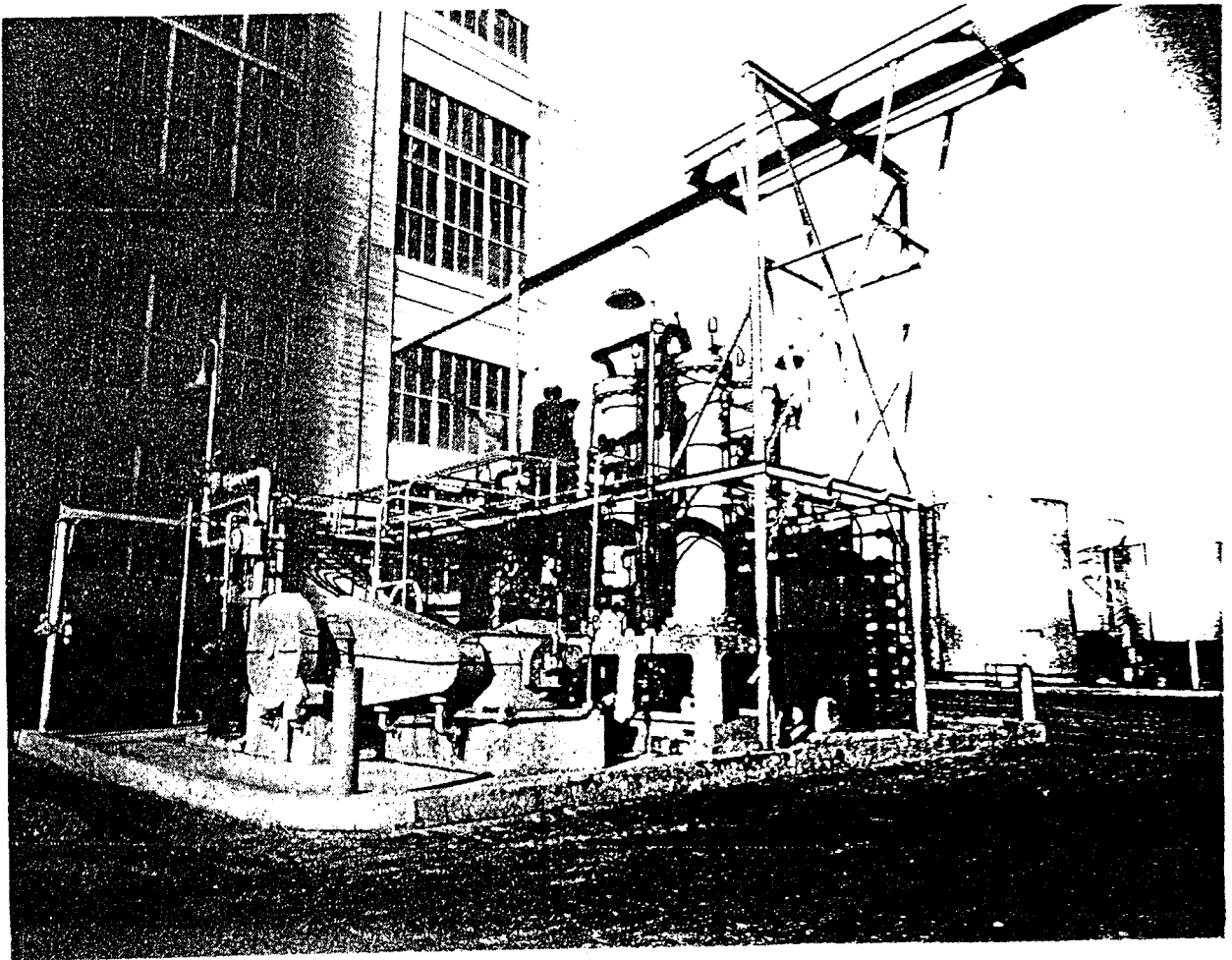


Fig. 2.6. Continuous hydrogenation unit (Procter & Gamble Co.)

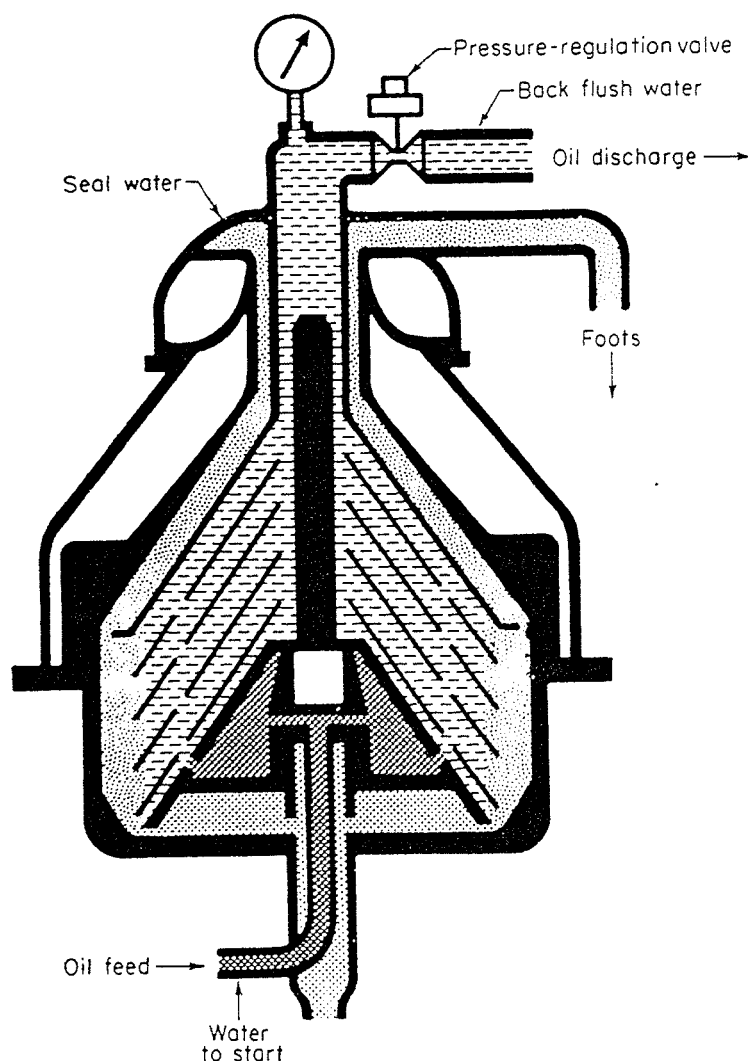


Fig. 2.7. Continuous separating centrifuge as used in the fatty-oil industry. (Procter & Gamble Co.)

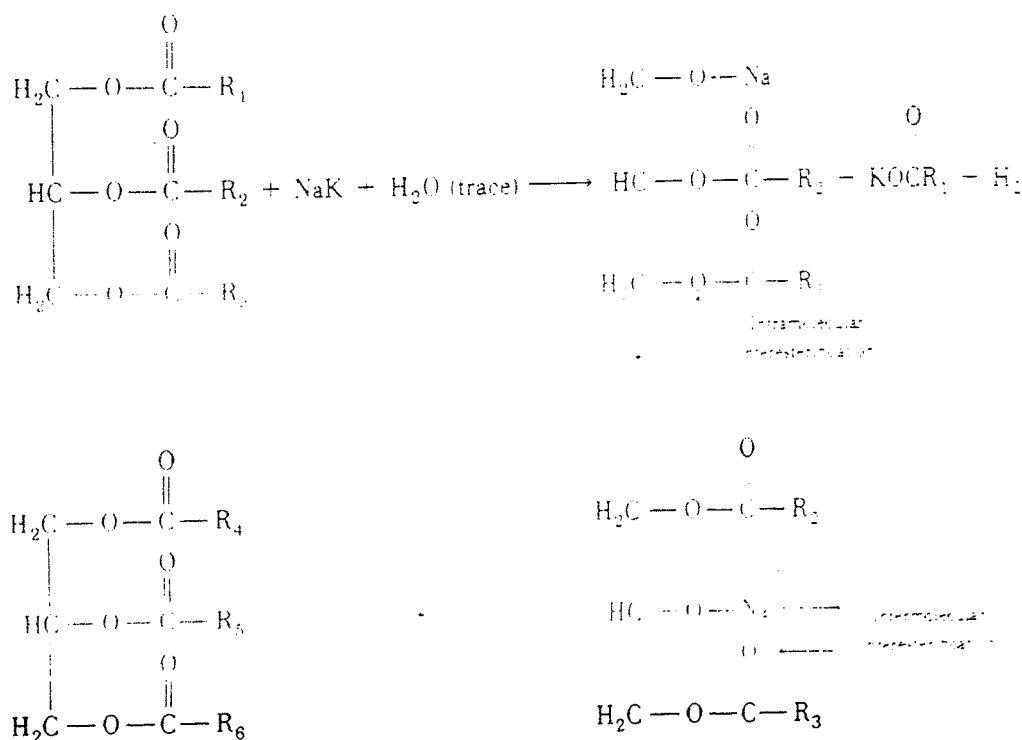
**INTERESTERIFICATION.** An advance in fat chemistry, which affected the overall amount of crude fats used in shortening manufacture, was the laboratory perfection and large-scale production of shortenings containing lard processed by random and directed interesterification.<sup>22</sup> For many years the blending of lard into good shortening was blocked by certain undesirable inherent characteristics of the lard. Lard has a grainy, translucent appearance and a short plastic range, or range of temperature, over which the fat is of good workability—neither too firm nor too soft. Graininess and short plastic range, however, require a chemical rearrangement of the lard fat glycerides for use in high-grade shortening. Graininess is due to the occurrence of a much greater than random proportion of disaturated triglyceride molecules containing stearic, palmitic, and unsaturated fatty acid chains. About 26 percent of lard triglycerides have this structure. The predominance of one particular type of triglyceride promotes the deposition of this fraction in large crystals over a short period of time. However, if lard is thoroughly dried and heated to 80°C for about 30 min with an alkaline catalyst

<sup>22</sup>Courtesy of Going, Procter & Gamble Co.; Hawley and Holman, Directed Interesterification as a New Processing Tool for Lard, *J. Am. Oil Chem. Soc.* 33 29 (1956); Placek and Holman, *Ind. Eng. Chem.* 49 162 (1957).

(sodium methoxide or Na-K alloy), the side chains will migrate among the glyceryl residues and, within minutes under the right conditions, will reach a random distribution. Neutralization of the catalyst stops the reaction. In such a randomizing process, the particular undesirable disaturated triglyceride structure is found to drop from 26 to about 3½%. Thus, by *randomizing*, the graininess of the lard is counteracted. Several commercial lard-based shortenings are produced<sup>23</sup> from such randomized lard.

Extending the plastic range of lard requires further processing. Most of the solids in lard or randomized lard are disaturated glycerides, which give shortening little or no heat resistance, since they melt at higher atmospheric temperatures. Ideally, a process is desired which uses disaturates to produce trisaturates and triunsaturates that do not change their physical state over the ambient temperature range but remain, respectively, solid and liquid. This has been found in what is termed *directed interesterification*.<sup>24</sup> If, in the presence of an active rearrangement catalyst, the randomized lard mass is chilled, fat solids in transient existence will irreversibly precipitate out. In cooling from the melt, the first solids to separate will be trisaturates. If the temperature is held slightly below the melting point of the trisaturates they will continue to separate so long as the constantly rearranging melt continues to rearrange saturated fatty acids into trisaturates in a futile attempt to reach equilibrium. Therefore the lard composition changes with time, and trisaturates and triunsaturates increase at the expense of mono- and disaturates. When the catalyst is neutralized, the composition remains frozen in the new form.

#### Interesterification reactions



<sup>23</sup>Going, U.S. Patent 2,309,949 (1943); Van der Wal et al., U.S. Patent 2,571,315 (1951) Holman et al., U.S. Patent 2,738,278 (1956).

<sup>24</sup>Eckey, U.S. Patents 2,422,531 and 2,442,532 (1948); Hawley, U.S. Patent 2,733,251 (1956); Holman et al., U.S. Patents 2,875,066 and 2,875,067 (1959).



These reactions proceed to a statistically random equilibrium of fatty acid combinations in the triglyceride molecules. In directed interesterification, a molecule crystallizes when its three fatty acids are saturated.

The flowchart in Fig. 2.8 presents the process steps in rearrangement. Dried lard is catalyzed with a sodium-potassium alloy, mixed, chilled in two stages, and crystallized. The end point is controlled by the cloud point. The reaction mass is neutralized and heated to separate the fat phase from the soap phase formed during neutralization of the catalyst.

## WAXES<sup>25</sup>

There are animal, vegetable, mineral, and synthetic waxes, depending upon the source. Animal waxes are secreted as protective coatings by certain insects. Vegetable waxes are found as coatings on leaves, stems, flowers, and seeds. Mineral waxes are paraffin waxes obtained from petroleum, and such waxes as are yielded by coal, peat, and lignite. Mineral waxes from petroleum are not true waxes (esters) but are so classified because of their physical characteristics.

**BEESWAX.** This is probably the best-known wax. It is made from honeycombs by solvent extraction, expression, or boiling in water. Many church candles contain more than 50% of this wax.

**CARNAUBA WAX.** This wax is obtained from the carnauba palm, which grows in Brazil. The leaves are cut, dried for 3 days, and sent to the beater house. The drying loosens the wax, which can be easily beaten from the slashed leaf, and it falls to the floor where it is gathered at the end of the day and melted. Less than 1 L of molten wax is obtained from 19 L of powdered wax. This is filtered through cheesecloth, allowed to harden, and sold. A palm tree produces about 90 g of wax per year. The product is used as a constituent of floor, automobile, and furniture polishes, and in carbon paper, candles, and certain molded products.

**SPERMACETI.** The oil removed from the head cavity, and parts of the blubber of the sperm whale is in reality a wax because of its chemical composition. Spermaceti is important for lubrication. The head oil, upon chilling and setting, is a solid wax. This constitutes about 11% of the original oil and is largely cetyl palmitate. It is melted, treated with a hot, dilute caustic soda solution, washed with water, and run into molds to solidify. It is translucent, odorless, and tasteless and is used chiefly as a base for ointments. By methylating sperm oil, Archer-Daniels-Midland has obtained a low surface tension (0.0017 to 0.0018 N/m) lubricant.

<sup>25</sup>Bennett, *Industrial Waxes*, 2d ed., Chem. Publ. Co., New York, 1975.

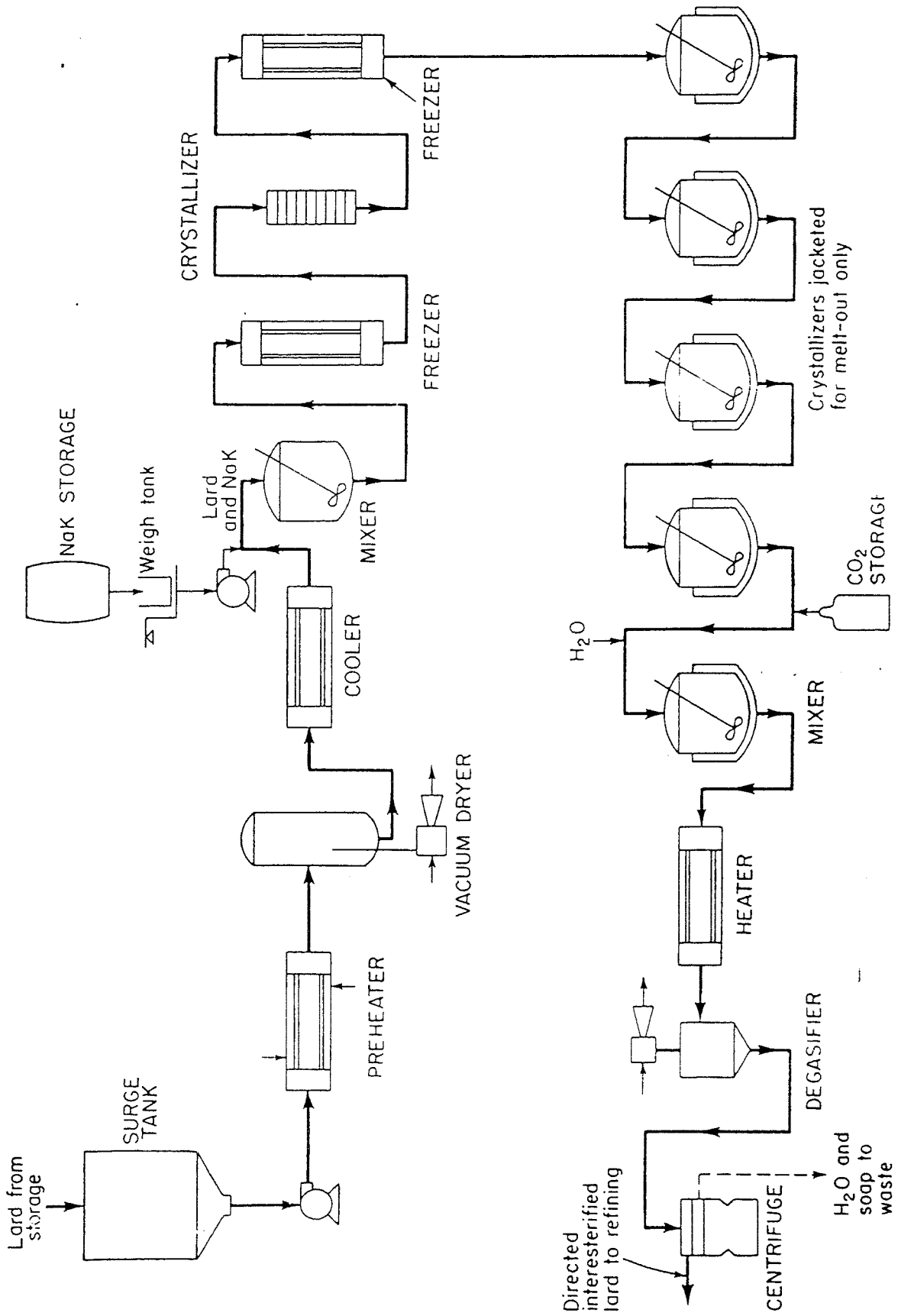


Fig. 2.8. Flowchart for continuous production of lard by direction interesterification. (Procter & Gamble Co.)

**OZOCERITE.** This is the name given to certain naturally occurring mineral waxes. The ozocerite known commercially is a particular earth wax mined in eastern Europe, but important similar waxes are mined elsewhere. One variety, mined in Utah, is known as Utahwax or Utah ozocerite. It can be substituted to a great extent for the other and is chiefly employed for electrical insulations, waterproofing, and impregnating.

**PARAFFIN WAX.** This wax is concentrated in certain lubricating-oil fractions as a result of distillation and is separated by chilling and filter-pressing (Chap. 37). Extraction of lube oil fractions with, e.g., a mixture of methyl ethyl ketone and benzene, followed by distillation into narrow-boiling fractions yields microcrystalline waxes.

**MONTAN WAX.** The name montan wax generally applies to the wax obtained from a bituminous wax solvent-extracted from bituminous lignite or shale, but a similar wax may be obtained from peat or brown coal. Its important applications include electrical insulations, polishes, and pastes.

**CANDELILLA WAX.** This is the third most important U.S. wax in tonnage and is made by boiling the stems of a plant common in Mexico and the southwestern United States with a water-sulfuric acid mixture and skimming off the wax which floats on the liquid. Another method of obtaining this wax is by extracting the stems with hexane and recovering the wax by distillation of the solvent.<sup>26</sup>

**SYNTHETIC WAXES.** Various materials are used to make synthetic waxes. Carbowaxes are high molecular weight polyethylene glycols. They are useful as wax emulsifiers, as well as being waxy themselves. Higher aliphatic alcohols are used as emulsified wax substitutes. Other synthetic waxes are produced from fatty acids and amines, and chlorinated paraffin waxes.

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<sup>26</sup>Chem. Eng. 87 (10) 85 (1980).

## Chapter 3

# Soap and Detergents

The washing industry, usually known as the soap industry, has roots over 2000 years in the past, a soap factory having been found in the Pompeii excavations. However, among the many chemical process industries, none has experienced such a fundamental change in chemical raw materials as have the washing industries. It has been generally accepted that the per capita use of toilet soap is a reliable guide to the standard of living for any country.

**HISTORICAL.** Soap itself was never actually “discovered,” but instead gradually evolved from crude mixtures of alkaline and fatty materials. Pliny the Elder described the manufacture of both hard and soft soap in the first century, but it was not until the thirteenth century that soap was produced in sufficient quantities to call it an industry. Up to the early 1800s soap was believed to be a mechanical mixture of fat and alkali; then Chevreul, a French chemist, showed that soap formation was actually a chemical reaction. Domeier completed his research on the recovery of glycerin from saponification mixtures in this period. Until Leblanc’s important discovery producing lower-priced sodium carbonate from sodium chloride, the alkali required was obtained by the crude leaching of wood ashes or from the evaporation of naturally occurring alkaline waters, e.g., the Nile River.

The raw material shortages of World War I led the Germans to develop “synthetic soaps” or detergents. These were composed of short-chain alkyl naphthalene sulfonates, which were good wetting agents but only fair in detergent action. This sparked the interest worldwide in developing detergents, and new developments are continuing to the present time. From the original short-chain compounds the development has progressed through long chain alcohol sulfates in the 1920s and 1930s, through alkyl-aryl long chain sulfonates in the 1940s, to branched chain compounds in the 1950s and 1960s. During the 1960s the requirement of biodegradability became important and caused the return to linear long chains, because only the linear chains can be easily biodegraded.

**USES AND ECONOMICS.**<sup>1</sup> In 1981 the total value of surfactant and soap shipments was \$10,701 million. Of this, the value of household soap shipments was about \$1300 million and for household detergent products, \$4000 million. Out of a total demand of 3200 kt, soap represented 39 percent with a demand of 540 kt and detergents accounted for 840 kt.<sup>1a</sup> Indus-

<sup>1</sup>U.S. *Industrial Outlook*, 1982, U.S. Dept. of Commerce; Layman, Surfactants—A Mature Market with Potential, *Chem. Eng. News* 60 (2) 13 (1982); Moffet and von Hennig, Detergent Activities, *Soap Cosmet. Chem. Spec.* 57 (9) 29 (1981); Piellisch, Stronger Than Dirt: The Battle of the Detergent Chemicals, *Chem. Bus.* June 29, 1981, p. 33.

<sup>1a</sup>t = 1000 kg; kt = 10<sup>6</sup> kg.



trial uses accounted for the difference. Figure 3.1 and Tables 3.1 and 3.3 show the gradual replacement of soap by detergents in the household market.

Laundry products, toilet soaps, shampoos, dishwashing products, and cleaning products are the chief household uses of these materials. Industrial uses include cleaning compounds, specialty surfactants for hospital germicides, fabric conditioners, emulsifiers for cosmetics, flowing and wetting agents for agricultural chemicals, and rubber processing aids. A potentially large use is for enhanced oil recovery from presently "worked-out" oil wells.

## DETERGENTS<sup>2</sup>

Detergents differ from soap in their action in hard water. Soaps form insoluble compounds with the calcium and magnesium ions present in hard water. These insoluble compounds precipitate out and reduce foaming and cleaning action. Detergents may react with the hard water ions, but the resulting products are either soluble or remain colloidally dispersed in the water. Table 3.2 illustrates the differences between soaps and detergents in composition and manufacture. Table 3.3 shows the consumption of surfactants in detergents.

Detergents have been divided into four main groups: anionic, cationic, nonionic, and amphoteric. The largest group consists of the anionics which are usually the sodium salts of

<sup>2</sup>Scientifically, the term detergent covers both soap and synthetic detergents, or "syndets," but it is widely used to indicate synthetic cleaning compounds, as distinguished from soap. It is so used in this book. The U.S. Tariff Commission reports on detergents under the name surface-active agents or surfactants under the broader class of synthetic organic chemicals.

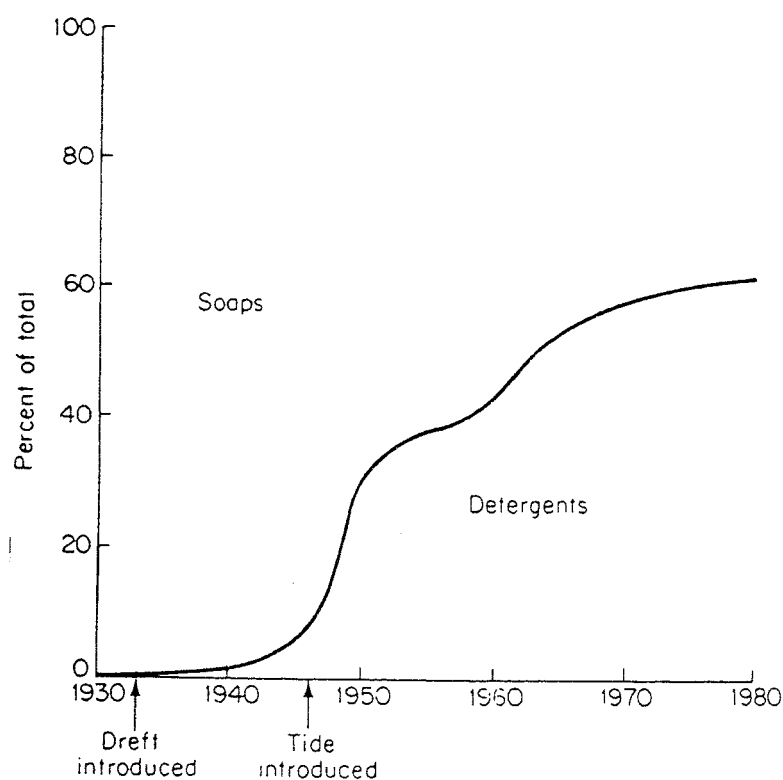


Fig. 3.1. Relative production of detergents and soap.

**Table 3.1** Production and Sales of Soaps and Surfactants

	Soap		Surfactants		Total	
	10 <sup>6</sup> \$	kt	10 <sup>6</sup> \$	kt	10 <sup>6</sup> \$	kt
1940	313	1455	7	13	320	1468
1945	527	1717	35	68	562	1785
1950	540	1308	294	655	834	1963
1960	376	558	953	1789	1329	2347
1970	427	567	1379	2563	1806	3132
1980	1030	545	8430	2663	9460	3208

SOURCE: CPI 4, chap. 29; *U.S. Industrial Outlook, 1982*, U.S. Dept. of Commerce.

an organic sulfate or sulfonate. Detergents can be formulated to produce a product of the desired characteristics ranging from maximum cleaning power, maximum cleaning unit of cost, to maximum biodegradability. Usually commercial products are a compromise of the various desirable properties.

Soil removal is accomplished by wetting, emulsifying, dispersing, and/or solubilizing the soil by the cleaning agent. Detergent molecules can aggregate in water into spherical clusters called micelles. The hydrocarbon parts of the molecules gather together on the inside of the micelle and the polar groups are on the outside. Oil-soluble water-insoluble compounds, such as dyes, are often dissolved into the center of the micelle attracted by the hydrocarbon groups. This process is known as solubilization.<sup>3</sup>

Detergents and soaps have water-attracting (hydrophilic) groups on one end of the molecule and water-repelling (hydrophobic) groups on the other. These special properties are used in soil removal.

During the 1960s and 1970s, the composition of detergents underwent rapid changes because of environmental considerations.<sup>4</sup> Evidence indicated that phosphates from deter-

<sup>3</sup>*McGraw-Hill Encyclopedia of Science and Technology*, 5th ed., vol. 12, McGraw-Hill, New York, 1982, p. 488.

<sup>4</sup>For Detergent Producers, the Question Is Which? *Chem. Week* 129:4-44 (1980)

**Table 3.2** Soaps and Detergents

To Make Synthetic Detergents
Alkylbenzene + oleum → alkylbenzene sulfonate
Tallow fatty alcohol + oleum → fatty alcohol sulfate
Sulfonate + sulfate + NaOH → sodium salts
Sodium salts + builders, etc. → detergents
To Make Soap
Tallow + hydrolysis (splitting fats) → tallow fatty acid
Tallow fatty acid + NaOH → sodium salt of fatty acid
Salt of fatty acid + builder, etc. → soap

**Table 3.3** Detergent Consumption of Surfactants (in metric kilotons)

	Powders	Liquids
Anionics		
Alkylbenzene sulfonate	145	40
Alcohol ethoxy sulfates	45	Small
Alcohol sulfates	23	—
Nonionics		
Alcohol ethoxylates	45	41
Alkyl phenol ethoxylates	5	5
Amines, amine oxides	5	5

SOURCE: *Chem. Week* 127:20-33 (1980)

gents may contribute to the eutrophication of lakes, so the use of phosphates in detergents was banned in some areas of the country. Many different substitutes were formulated into detergents, but some of these were found to be unsafe and were then banned. The position taken by the detergent industry has been that phosphates in wastewater can be removed by special treatment in sewage plants and, in view of the proved lack of toxicity of phosphates, their replacement may not be the most desirable solution. The soap and detergent industry and its suppliers face an enormous task in testing new materials for all possible effects on the environment, and extensive research will be needed before this complex problem can be solved.

## Raw Materials

A large volume of active organic compounds, or surfactants,<sup>5</sup> for both detergents and soap are manufactured in final form by soap and detergent companies. Examples are linear alkylbenzene sulfonate (LAS) and fatty alcohol sulfate, which these companies manufacture in hundreds of millions of pounds. The same is true for fatty acids, the basic materials for soaps. Most of the inorganic materials, such as oleum, caustic soda, and various sodium phosphates and a large number of additives, the last mentioned amounting to 3% or less of the total product weight are purchased.

**SURFACTANTS.** These embrace "any compound that affects (usually reduces) surface tension when dissolved in water or water solutions, or which similarly affects interfacial tension between two liquids. Soap is such a material, but the term is most frequently applied to organic derivatives such as sodium salts of high molecular weight alkyl sulfates or sulfonates."<sup>6</sup> The surfactants of both soap and synthetic detergents perform the primary cleaning and sudsing of the washing action in the same way through the reduction of surface tension. The cleaning process consists of (1) thoroughly wetting the dirt and the surface of the article being washed with the soap or detergent solution, (2) removing the dirt from the surface, and (3) maintaining the dirt in a stable solution or suspension (detergency). In wash water, soaps or detergents increase the wetting ability of the water so that it can more easily penetrate the fabrics and reach the soil. Then soil removal begins. Each molecule of the cleaning solution may be considered a long chain. One end of the chain is hydrophilic (water-loving); the other is hydrophobic (water-hating, or soil-loving). The soil-loving ends of some of these molecules are attracted to a soil particle and surround it. At the same time the water-loving ends pull the molecules and the soil particles away from the fabric and into the wash water. This is the action which, when combined with the mechanical agitation of the washing machine, enables a soap or detergent to remove soil, suspend it, and keep it from redepositing on clothes.

**Classification.** In most cases the hydrophobic portion is a hydrocarbon containing 8 to 18 carbon atoms in a straight or slightly branched chain. In certain cases, a benzene ring may replace some of the carbon atoms in the chain, for example,  $C_{12}H_{25}-$ ,  $C_9H_{19}\cdot C_6H_4-$ . The hydrophilic functional group may vary widely and may be anionic, e.g.,  $-OSO_4^-$  or  $SO_3^{2-}$ ; cationic, e.g.,  $-N(CH_3)_3^+$  or  $C_5H_5N^+$ ; or nonionic, e.g.,  $-(OCH_2CH_2)_nOH$ .

In the anionic class one finds the most used compounds, namely linear alkylbenzene sulfonates from petroleum and alkyl sulfates from animal and vegetable fats (Fig. 3.2). Soap is

<sup>5</sup>Abbreviation for surface-active agents.

<sup>6</sup>Rose, *The Condensed Chemical Dictionary*, 6th ed., Reinhold, New York, 1961.

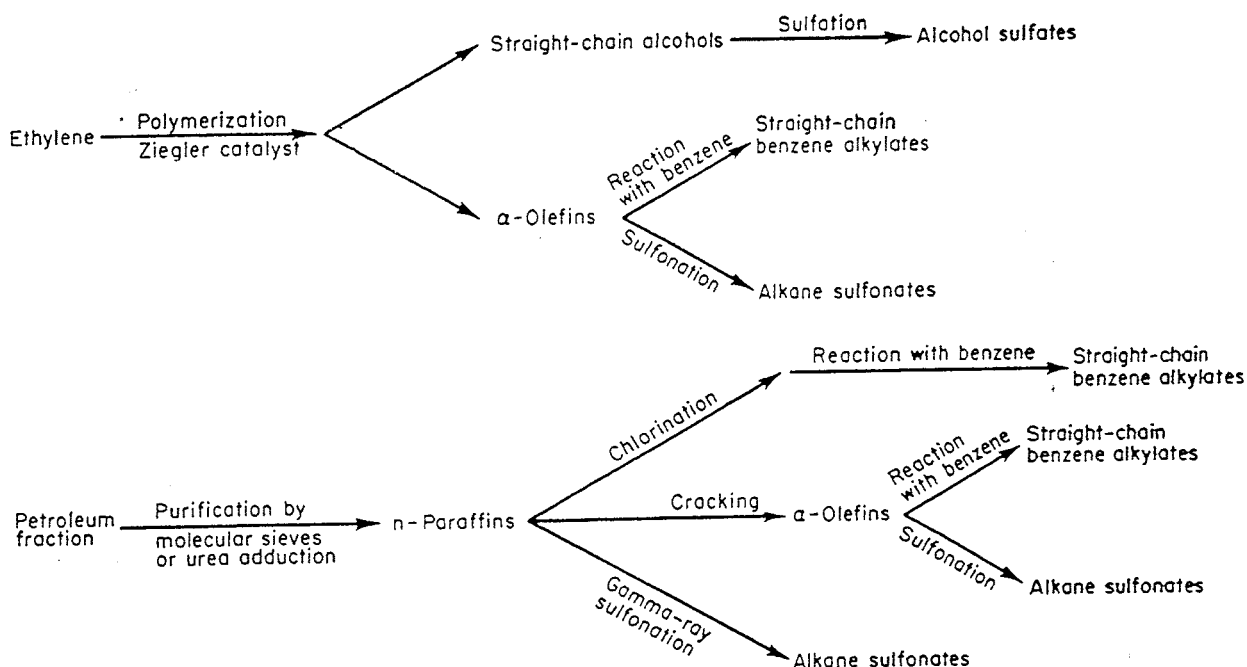
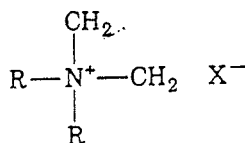
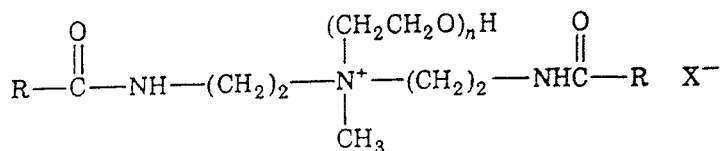


Fig. 3.2. Some possible paths to soft-detergent components. [*Chem. Eng.* 70 (18) 25 (1963).]

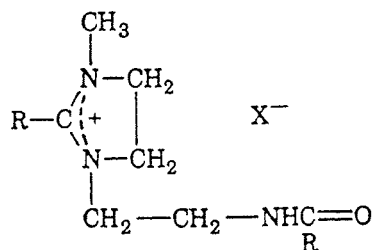
also anionic in character. Quaternary ammonium compounds comprise the cationic class. Three general types are used, mainly for fabric softeners. Type A is a dialkyl dimethyl quaternary ammonium compound



where  $\text{X}^-$  is either  $\text{Cl}^-$  or  $\text{CH}_3\text{SO}_4^-$ . Type B is a diamido alkoxyated quaternary ammonium compound, where  $\text{X}^-$  is  $\text{CH}_3\text{SO}_4^-$ .



Type C<sup>7</sup> is an amido imidazolinium compound where  $\text{X}^-$  is  $\text{CH}_3\text{SO}_4^-$ .



<sup>7</sup>Williams, How to Choose Cationics for Fabric Softeners, *Soap Cosmet. Chem. Spec.* 58 (8) 28 (1982).

Being generally weak in detergent power, although they have good lubricating, antistatic, and germicidal properties, they are not usually used as household detergents. Anionics and cationics are not compatible with soap.

Ethylene oxide condensates of fatty alcohols illustrate the molecular structure of nonionic surfactants. There are many excellent soil-removing types that are low sudsers and hence are useful in drum-type automatic clothes washers. Nonionics are more effective than anionics in removing soil at the lower temperatures necessary for laundering synthetic fibers. They are also more effective at removing body oils.

**Biodegradability.**<sup>8</sup> In view of the attention being given to water pollution control and abatement, product-development chemists and chemical engineers have realized that surfactants being developed for use in household and industrial detergents that go down the drain to the sewer must be readily decomposable to inorganic compounds by the microbial action of sewage treatment and in surface streams. This new parameter has been added to the performance, efficiency, and cost factors the detergent industry must consider in developing new products. Some surfactants, like tetrapropylene-derived alkylbenzene sulfonate, degrade slowly, leaving a persistent residue. Others are more readily decomposable by microorganisms and leave practically no persistent residues. The ease with which a surfactant is decomposed by microbial action has been defined as its biodegradability. Tests are being developed and standards are being established for biodegradability. To have broad application, such standards must recognize the breadth of variation in environmental conditions. Materials which may be only partly degraded in inefficient treatment processes can be completely decomposed by more sophisticated biological treatment systems. Methods of testing radiolabeled surfactants of anionic, cationic, and nonionic types and builders have been developed to determine the rate of biodegradation in parts per billion in natural waters and also to determine if threshold concentrations, below which degradation is not observed, exist.<sup>9</sup>

**STRAIGHT-CHAIN ALKYL BENZENES.** Biodegradable detergents are made primarily from phenyl-substituted *n*-alkanes of 11 to 14 carbon atoms. The straight-chain paraffins or olefins needed are produced from petroleum as shown in Fig. 3.2. In 1981, 233 kt were produced in the United States.

*n*-Alkanes are separated from kerosene by adsorption using molecular sieves. Branched chain and cyclic alkanes have larger cross-sectional diameters than do the linear molecules, thus making sieve separation possible. The other common method of separation of the normal paraffin compounds from the branched and cyclic ones is by reaction with urea or thiourea. Urea will react with linear chain hydrocarbons having at least seven carbon atoms to give a crystalline adduct which is separable by filtration. No such adduct is formed with the branched chain or cyclic compounds. The adduct can then be decomposed by heating with hot water at 80 to 90°C. Conversely, thiourea will react with the branched chain hydrocarbons but will not form adducts with straight-chain or aromatic ones. The separated *n*-paraffins are converted to benzene alkylates or are cracked to yield  $\alpha$ -olefins.

Linear olefins are prepared by dehydrogenation of paraffins, by polymerization of ethylene to  $\alpha$ -olefins using an aluminum triethyl catalyst (Ziegler-type catalyst), by cracking paraffin wax, or by dehydrohalogenation of alkyl halides.

<sup>8</sup>Larson, "Role of Biodegradation Kinetics in Predicting Environmental Fate," in Maki, Dickson, and Cairns (ed.), *Biotransformation and Fate of Chemicals in the Aquatic Environment*, Am. Soc. for Microbiol. Publ., Washington, D.C., 1980.

<sup>9</sup>Larson and Wentler, Biodegradation of Detergent Materials, *Soap Cosmet. Chem. Spec.* 58 (5) 53 (1982).

$\alpha$ -Olefins or alkane halides can be used to alkylate benzene through the Friedel-Crafts reaction, employing hydrofluoric acid or aluminum fluoride as a catalyst.

### FATTY ACIDS AND FATTY ALCOHOLS

**Economics.** Fatty alcohols and fatty acids are mainly consumed in the manufacture of detergents and soaps. Fatty acids, both saturated (e.g., stearic acid) and unsaturated (e.g., oleic), have long been employed in many industries as both free acids, and, more frequently, as salts. Examples are:

Magnesium stearates in face powders.

Calcium or aluminum soaps (insoluble) employed as water repellents in waterproofing tiles and walls.

Triethanolamine oleate in dry cleaning and cosmetics.

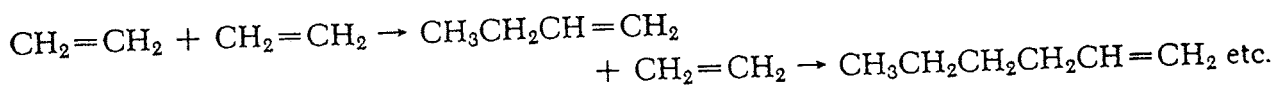
Lithium stearate as a component of greases.

Rosin soap consumed as a sizing for paper.

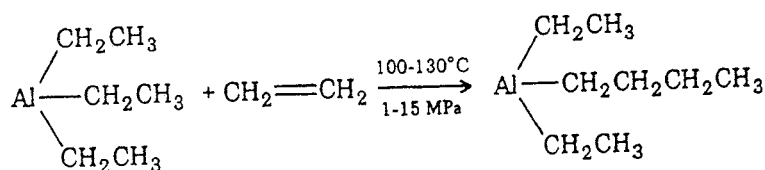
**Manufacture of Fatty Acids.**<sup>10</sup> Basic raw materials, such as oils and fats, which have been used for a long time (Chap. 2), have, since about 1955, been very extensively supplemented by improved chemical processing and by synthetic petrochemicals. A selection from these processes is given here. Table 3.4 compares three processes for splitting fats that have been used for many years. Figure 3.3 illustrates the high-pressure hydrolysis, catalyzed by zinc oxide, which is used in the soap industry. Fatty acids are drawn off from the distillate receiver for sale or for further conversion to fatty acid salts (calcium, magnesium, zinc, etc.). Several older and less used separation methods for purifying fatty acids are panning and pressing, fractional distillation, and solvent crystallization.

**Manufacture of Fatty Alcohols.** The Ziegler catalytic procedure for converting  $\alpha$ -olefins to fatty alcohols and the methyl ester hydrogenation process are the important methods for preparing fatty alcohols. See also the flowchart in Fig. 3.4 and the text presented under soap for the continuous hydrolysis of fats to furnish fatty acids which may be hydrogenated to fatty alcohols.

The Ziegler<sup>11</sup> procedure is an important one for manufacturing  $C_{12}$  to  $C_{18}$   $\alpha$ -olefins and fatty even-numbered straight-chain alcohols for detergents. See Fig. 3.4. Gaseous ethylene is converted to higher, linear aluminum trialkyls and  $\alpha$ -olefins by the action of aluminum triethyl which takes part in the reactions.



### CHAIN GROWTH REACTION



<sup>10</sup>ECT, 3d ed., vol. 4, 1978, p. 837.

<sup>11</sup>Sittig, *Detergent Manufacturing*, Noyes, Park Ridge, N.J., 1979; ECT, 3d ed., vol. 1, 1978, p. 740.

**Table 3-4** Tabular Comparison of the Various Fat-Splitting Processes

	Twitchell	Batch autoclave		Continuous Countercurrent*
Temperature, °C	100–105	150–175	240	250
Pressure, MPag		5.2–10.0	2.9–3.1	4.1–4.9
Catalyst	Alkyl-aryl sulfonic acids or cycloaliphatic sulfonic acids, both used with sulfuric acid 0.75–1.25% of the charge	Zinc, calcium, or magnesium oxides, 1–2%	No catalyst	Optional
Time, h	12–48	5–10	2–4	2–3
Operation	Batch	Batch		Continuous
Equipment	Lead-lined, copper-lined, Monel-lined, or wooden tanks	Copper or stainless-steel autoclave		Type 316 stainless tower
Hydrolyzed	85–98% hydrolyzed 5–15% glycerol solution obtained, depending on number of stages and type of fat	85–98% hydrolyzed 10–15% glycerol, depending on number of stages and type of fat		97–99% 10–25% glycerol, dependent on type of fat
Advantages	Low temperature and pressure; adaptable to small scale; low first cost because of relatively simple and inexpensive equipment	Adaptable to small scale; lower first cost for small scale than continuous process; faster than Twitchell		Small floor space; uniform product quality; high yield of acids; high glycerin concentration; low labor cost; more accurate and automatic control; lower annual costs
Disadvantages	Catalyst handling; long reaction time; fat stocks of poor quality must often be acid-refined to avoid catalyst poisoning; high steam consumption; tendency to form dark-colored acids; need more than one stage for good yield and high glycerin concentration; not adaptable to automatic control; high labor cost	High first cost; catalyst handling; longer reaction time than continuous processes; not so adaptable to automatic control as continuous; high labor cost; need more than one stage for good yield and high glycerin concentration		High first cost; high temperature and pressure; greater operating skill

SOURCE: Mostly from Marsel and Allen, Fatty Acid Processing, *Chem. Eng.* **54** (6) 104 (1947). Modified in 1982.

\*See Fig. 29.8.